

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Alcohols.

We, CELANESE CORPORATION OF AMERICA, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with 5 the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of hydroxy compounds by the hydrogenation of esters, including lactones. 15 The present invention provides a process for the hydrogenation of an ester, including a lactone, to the corresponding monohydric or dihydric alcohols by reaction with hydrogen at an elevated temperature and under superatmospheric pressure in the presence of an active copper hydrogenation catalyst comprising Raney copper or barium oxide promoted copper chromite.

In accordance with the process according 25 to the invention, the products of an ester of a carboxylic acid comprise the alcohol component of the ester together with an alcohol corresponding to and having the same number of carbon atoms as the acid component of the ester. Where the ester is a simple intermolecular product derived from separate alcohol and acid molecules, then both alcohol products of the hydrogenation may be monohydric; according to the 30 ester selected they may comprise the same alcoholic species. Thus, both parts of n-hexyl caproate will yield n-hexanol. Where however the ester is internal or intramolecular i.e. a lactone, then only a single alcohol product can be formed which is necessarily a dihydric alcohol.

The acyl portion of the ester to be hydrogenated may be derived from a mono- or

poly-basic aliphatic saturated acid having 12 or fewer carbon atoms. In the acyclic esters the alcoholic moiety may be derived from a mono- or poly-hydric aliphatic alcohol containing the same or a different number of carbon atoms from the acyl portion of the molecule e.g. 1,6-hexanediol, n-hexanol, cyclohexanol, 1,4-butanediol, n-octanol or the like. The lactones which may be used may contain up to 8 carbon atoms and preferably contain at least 4 carbon atoms, e.g. butyrolactone, gamma-valerolactone and epsilon-caprolactone. The lactone ring may have non-hydrogen absorbing substituents thereon if desired. It is within the scope of the invention to hydrogenate esters having hydroxyl groups on the acyl portion of the molecule, e.g. 1,6-hexanediol mono- or di(hydroxy caproate), and amino esters, e.g. hexyl (6 amino) caproate.

The process may be carried out by feeding the compound to be hydrogenated and hydrogen to a reactor maintained at an elevated temperature, e.g. 200 to 350°C. and under superatmospheric pressure, e.g. a gauge pressure of 1000 to 12,000 pounds per square inch, the preferred temperatures being 250 to 290°C. and the preferred gauge pressures being 3700 to 5000 pounds per square inch. Where copper chromite type catalysts are used, they are preferably supported on pumice or inactive alumina, the latter being alumina hydrate which has been calcined at between about 1000°C. and the melting point of alumina. It is practical to carry out the hydrogenation either with or without a solvent. Where a solvent is used, dioxane has been found to work well as have butanol and ethanol. The solvent may be mixed with the compound to be hydrogenated, e.g. at 100 to 150°C., the mixture then heated, e.g. to 190°C., in a closed vessel and then fed into the hydrogenation re-

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- actor. The proportion of solvent to ester in the feed may be, for instance, from 1:4 to 2:1 and is preferably about 1:1. Whether or not a solvent is used, with such preheating temperatures the heat of reaction usually brings the reaction mass up to a temperature of about 245 to 250°C. and the feed hydrogen supplies the pressure necessary for hydrogenation.
- The hydrogenation reaction can be carried out in either a fixed, flooded catalyst bed, a slurry catalyst bed, or a trickle catalyst bed. A fixed, flooded catalyst bed is one in which the particles of catalyst are substantially pelletized or in some other relatively large form, while the compound being hydrogenated and any solvent used forms a continuous liquid phase which completely submerges the catalyst. A fixed trickle catalyst bed is one in which the particles of catalyst are generally pelletized and in a relatively fixed position with the compound being hydrogenated and any solvent being fed at the top of the bed and forming a relatively discontinuous phase. A slurry bed catalyst consists of powdered catalyst, e.g. about 60 microns or less, suspended in the liquid phase. In a slurry bed type catalyst it is usual to introduce the liquid at the bottom of the bed, in the trickle bed catalyst it is usual to introduce the liquid at the top of the catalyst bed and in the flooded, fixed bed catalyst the liquid can conveniently be fed at top or bottom, although the bottom is preferred. In each case the gas phase is introduced at the bottom of the catalyst bed.

With the copper hydrogenation catalysts a catalyst life corresponding to more than 100 pounds, e.g. 200 pounds, of alcohol hydrogenation product per pound of catalyst can be achieved.

The following Examples, in which all proportions are in parts by weight or weight percent unless specified to the contrary, illustrate the invention:

Example 1

A stream containing 666 parts per hour of 1,6-hexanediol esters of adipic and epsilon-hydroxycaproic acids was fed, with 74 parts per hour of hydrogen, to a hydrogenation reactor containing barium oxide promoted copper chromite. The reactor was maintained at 260 to 275°C and under a gauge pressure of 4000 to 4800 pounds per square inch. The residence time of the reactants was 3 hours. The hydrogenation product contained 74% 1,6-hexanediol.

Example 2

Ethyl pelargonate was hydrogenated in a fixed bed reactor using a Raney copper catalyst. The catalyst was prepared by leaching 10 weight percent of the aluminium out of a copper-aluminium alloy crushed to pass a $\frac{1}{4}$ inch mesh screen. The reactor was operated as a trickle bed reactor at an ester feed rate of 11 parts per hour per cubic foot of catalyst under a gauge pressure of 4000 pounds per square inch and at a temperature of 260°C. After 1.7 hours of operation, the product contained 56.4% nonyl alcohol. The conversion rate was 7.3 parts of ester per hour per cubic foot of catalyst.

Example 3

Epsilon-caprolactone was fed into a hydrogenation reactor at 31 parts per hour per cubic foot of reactor volume under a gauge pressure of 4000 pounds per square inch at a temperature of 250°C. The catalyst was Raney copper prepared as in Example 2. After 5 hours of operation, 89% of the caprolactone was converted to 1,6-hexanediol.

WHAT WE CLAIM IS:—

1. Process for the hydrogenation of an ester, including a lactone, to the corresponding monohydric or dihydric alcohols by reaction with hydrogen at an elevated temperature and under superatmospheric pressure in the presence of an active copper hydrogenation catalyst comprising Raney copper or barium oxide promoted copper chromite. 85
2. Process according to Claim 1, wherein the catalyst comprises barium oxide promoted copper chromite supported on inactive alumina. 95
3. Process according to Claim 2, wherein the hydrogenation is carried out under a gauge pressure of 3700 to 5000 pounds per square inch and a temperature of 250 to 290°C. 100
4. Process for the production of a monohydric or dihydric alcohol substantially as described. 105
5. Process for the production of 1,6-hexanediol substantially as described in the examples. 110
6. Monohydric and dihydric alcohols whenever produced by any of the processes claimed in the preceding claims. 110

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